Thermal Effects on Liquefaction of Kentucky #9 Coal with $NiMo/AL_2O_3$ Catalyst

K. C. Kwon

Chemical Engineering Department
Tuskegee University
Tuskegee, Alabama 36088

Introduction

The main objectives of this research are (1) to investigate effects of heating rates on deactivation of catalysts, (2) to identify interactions between hydrogen donor solvents (HDS) and catalysts, (3) to study effects of initial temperatures on catalytic activities, and (4) to elucidate interactions between physical solvents and catalytic activities in the early stage of coal liquefaction.

A series of liquefaction experiments were conducted for Kentucky #9 coal (Ky #9 coal) without hydrogen donor solvents in the presence of presulfided fresh Shell 324 M catalyst, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min (4,5). Naphthalene (NAP) was hydrogenated with molecular hydrogen in the presence of used catalysts to evaluate catalytic activities of used catalysts. Liquefaction of Ky #9 coal decreases and catalytic activities increase, as heating rates increase, as shown in Figure 1. The initial liquefaction temperatures appear to affect liquefaction of Ky #9 coal in the presence of presulfided fresh Shell 324 M catalyst, whereas catalytic activities appear to be independent of the initial temperatures in the absence of hydrogen donor solvents.

When hexadecane (HEX) was used instead of 1-methylnaphthalene (1-MN) as a physical solvent, both liquefaction of Ky #9 coal and deactivation of Shell 324 M (NiMo) catalyst are less in the presence of Hex than 1-MN.

Another series of liquefaction runs of Ky #9 coal were performed in the presence of both presulfided fresh Shell 324 M catalyst and various hydrogen donor solvents such as anthracene (AN), 9,10-dihydroanthracene (DHA), phenanthrene(PN), 9,10-dihydrophenanthrene(DHP), quinoline(Q), and 1,2,3,4-tetrahydroquinoline(THQ) (1, 2, 6, 7). The liquefaction temperature was increased from 200°C or 300°C up to 380°C in the heating rates of 1-6°C/min.

Liquefaction of Ky #9 coal decreases, as heating rates increase, as shown in Figures 3 through 6. The initial liquefaction temperatures appear to affect both liquefaction of Ky #9 coal and deactivation of Shell 324 M catalyst in the early stage of liquefying Ky #9 coal in the presence of hydrogen donor solvents. Deactivation of Shell 324 M catalyst appears to decrease with increasing heating rates. On the other hand, the initial temperatures appear to affect liquefaction of Ky #9 coal and seem not to affect deactivation of Shell 324 M catalyst in the absence of hydrogen donor solvents.

Experimental

Coal liquefaction runs were conducted, using Ky #9 coal. Either hexadecane or 1-MN was utilized as a physical solvent. A 13 cc, 316 stainless steel microreactor was fed with 1 g coal, 0.1 g hydrogen donor solvent, 2.9 g physical solvent, 0.1 g presulfided fresh Shell 324 M catalyst and 1200 psig hydrogen at room temperature, as shown in Table 1. Q, THQ, AN, DHA, PN, and DHP were introduced in the reactor as hydrogen donor solvents. Liquefaction temperatures were increased from 200°C or 300° C up to 380°C and held at 380°C for 15 min.

Following coal liquefaction at the desired reaction time and temperature, the reactor was quenched in cold water and the gaseous products were released. The liquid-and-solid liquefaction products as well as the used catalyst were removed completely from the reactor by dissolving these liquefaction products with tetrahydrofuran(THF). The catalyst was separated from the solid-and-liquid liquefaction products and then was washed with 200 cc THF by sonicating the spent catalyst in THF for 12 min.

The liquefaction products were separated into a THF soluble fraction, a toluene-insoluble fraction and a cyclohexane-insoluble fraction to obtain a product distribution in terms of preasphaltene(PRA), asphaltene(ASP) and oil-plus-water-plus-gas (OWG) (8).

Naphthalene was hydrogenated with molecular hydrogen in the presence of the sonicated spent catalyst to examine deactivation of spent catalyst, as shown in Table 2.

Conversions of hydrogen donor solvents were analyzed, using a gas chromatograph, equipped with a flame-ionization detector and an 8 ft. long, 1/8 inch OD, SP 2100 packed column.

Discussions

A series of Ky #9 coal liquefaction runs were carried out without hydrogen donor solvents, in the presence of presulfided fresh Shell 324 (NiMo) catalyst, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min., as shown in Figure 1.

Coal liquefaction decreases with increasing heating rates and levels off at high heating rates. Deactivation of catalyst also decreases with increasing heating rates. The initial temperatures appear to affect liquefaction of Ky #9 coal, whereas the initial temperatures do not appear to affect deactivation of catalyst in the early stage of liquefying Ky #9 coal in the absence of hydrogen donor solvents. Figure 1 shows that liquefaction of Ky #9 coal in the absence of HDS significantly takes place at low heating rates and does not take place at high heating rates between liquefaction temperatures 200°C and 300°C. These data also suggest that deactivation of catalyst in the absence of HDS does not appear to occur significantly between liquefaction temperatures 200°C and 300°C.

When hexadecane as a physical solvent was used instead of 1-MN, both liquefaction of Ky #9 coal and deactivation of catalyst were lower in the presence of hexadecane than 1-MN in liquefying Ky #9 coal in the absence of hydrogen donor solvents, as shown in Figure 1. These facts may indicate that both liquefaction of Ky #9 coal and deactivation of catalyst in the absence of HDS are affected by physical solvents.

Another series of coal liquefaction runs of Ky #9 coal were carried out in the presence of both presulfided fresh Shell 324 M catalyst and various hydrogen donor solvents such as AN, DHA, PN, DHP, Q, and THQ, using 1-MN as a physical solvent. The liquefaction temperature was increased from 200°C or 300°C up to 380°C in the heating rates of 1-6°C/min, as shown in Figures 2 through 6.

Both liquefaction of Ky #9 coal and deactivation of catalyst decrease with increasing heating rates. The initial temperatures affect both liquefaction of Ky #9 coal and deactivation of catalyst in the presence of HDS. These observations may explain that both liquefaction of Ky #9 coal and deactivation of catalyst take place in the presence of HDS between liquefaction temperatures 200°C and 300°C.

Ky #9 coal was liquefied more in the presence of hydroaromatics such as DHA and DHP than corresponding aromatics such as AN and PN between liquefaction temperatures 200°C and 300°C, as shown in Figures 2, 3 and 6. These facts may elucidate that availability of donative hydrogen from hydrogen donor solvents is quite important in the early stage of liquefying Ky #9 coal in the presence of NiMo catalyst (3).

Deactivation of catalyst significantly takes place in the early stage of liquefying Ky #9 coal in the presence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figures 2 through 6, whereas deactivation of catalyst does not appear to take place in the early stage of liquefying Ky #9 coal in the absence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figure 1. These facts may indicate that hydrogen donor solvent itself appears to contribute to deactivation of catalyst in the early stage of liquefying Ky #9 coal.

Liquefaction of Ky #9 coal in the presence of Q decreases less with increasing heating rates than that in the presence of THQ. Deactivation of catalyst in the presence of Q decreases with increasing heating rates, whereas deactivation of catalyst in the presence of THQ decreases and then increases with increasing heating rates, as shown in Figures 4 and 5. This observation may suggest that THQ as a hydrogen donor solvent appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal.

Effects of various hydrogen donor solvents on liquefaction of Ky #9 coal were compared on a THF-solubles-vs-heating rates plot, as shown in Figure 6. The THF solubles-vs-heating rates curves for AN, DHA, Q and THQ are concave upward, whereas THF-soluble-vs-heating rates curves for PN and DHP are concave downward. Effects of heating rates on liquefaction of Ky #9 coal in the presence of quinoline appear to be least among others. These observations may indicate that characteristic plots of THF-solubles-vs-heating rates data are dependent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst.

Conclusions

The following conclusions were made on the basis of the available data in this research.

- Initial temperatures appear to affect liquefaction of Ky #9 coal, whereas initial temperatures do not appear to affect deactivation of Shell 324 M (NiMo) catalyst in the early stage of liquefying Ky #9 coal in the absence of hydrogen donor solvents (See Figure 1)

- Physical solvent itself appears to affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the absence of HDS. (See Figure 1)

- Initial temperatures affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the presence of HDS. (See Figures 2 through 5)

- Hydrogen donor solvent itself appears to contribute to catalytic deactivation in the early stage of liquefying Ky #9 coal. (See Figures 1 vs Figures 2 through 5)

- Characteristic plots of THF-soluble-vs-heating-rate data are dependent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst

- Quinoline behaves as a hydrogen donor solvent least sensitive to heating rates among others and THQ appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst and 1-MN as a physical solvent

- Coal liquefaction as well as catalytic deactivation can be identified, estimated and compared over a desired temperature range of coal liquefaction by liquefying coals at nonisothermal liquefaction temperatures

Acknowledgements

This research was supported by the U. S. Department of Energy through the contract number DE-FG22-84PC70802.

Literature References

1. Curtis, Christine W., James A. Guin and K. C. Kwon, "Coal Solvolysis in a Series of Model Compound Systems", Fuel, Vol. 62, P. 1341, 1983.

2. Derbyshire, F. J., G. A. Odoerfer and D. D. Whitehurst, "coal Liquefaction in Nitrogen Compounds", Fuel, Vol. 63, P. 57, 1983.

3. Guin, James A., Christine W. Curtis and K. C. Kwon, "Pyrite Catalyzed Coal liquefaction using Quinoline/Tetrahydroquinoline as a H-Donor System".

4. Mohan, Govindan and Harry Silla, "Kinetics of Donor Solvents Liquefaction of Bituminous Coals in Nonisothermal Experiments", Ind. Eng. Chem. Process Design and Development, 20, P. 349, 1981.

5. Okutani Takeshi and Nell R. Foster, "Novel Kinetic Analysis of Coal Liquefaction", Ind. Eng. Chem. Fundam., Vol. 22, P. 308, 1983.

6. Padrik, T. D., Lynch, A. W. and Stephens, H. P., "Effects of Solvent on the Dissolution of Wyodak Coal", Procedings of the Department of Energy Integrated Two-Stage Liquefaction Metings, Albuquerque, New Mexico, October, 1982.

7. Utz, B. R., H. R. Appell and B. R. Blaustein, "Vehicle Studies in Short Contact Time Liquefaction", Procedings of the Department of Energy Integrated Two-Stage Liquefaction Meetings, P. 17-1, Alburquerque, New Mexico, 1982.

8. Utz, B. R., Narain, N. K., Appell, H. R. and Blaustein, B. D., "Solvent Analysis of Coal Derived Products, Using Pressure Filtration", Am. Chem. soc. Symp. Ser., Edited by Fuller, American Chemical Society, Washington, D.C.

Table 1

Liquefaction Conditions of Ky #9 Coal

Initial Temperatures (I.T.)	(°C):	200 or 300
Final Temperature	(°C):	380
Heating Rate (°C/Min)	:	1-6
Liquefaction Duration at 380°C (Min)	:	0 or 15

Reactor Charge

Hydrogen(H_2)	:	1200 psig at room temperature
Coal	:	1 g
Physical Solvent	:	2.9 g or 3 g 1-Methylnaphthalene or 3 g Hexadecane
Hydrogen Donor Solvent	:	0.1 g
Presulfided Fresh Shell 324 M Catalyst	:	0.1 g

Table 2

Reaction Conditions of Evaluating Deactivation of Catalyst

Reaction Temperature	:	380°C
Reaction Duration	:	15 min.

Reactor Charge

Naphthalene	:	0.1 g
Hydrogen	:	1200 psig at room temperature
Used Catalyst	:	0.1 g
Hexadecane	:	2.9 g

Figure 1

Effects of Heating Rates on liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the absence of HDS, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min.

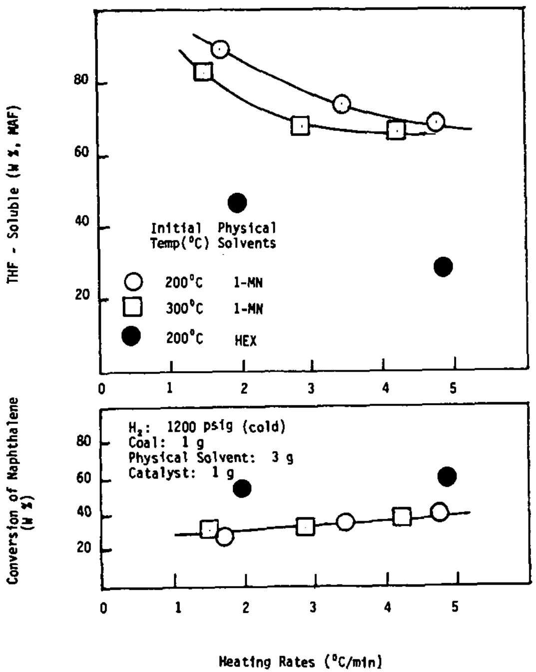

Figure 2

Effects of Heating Rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of AN, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

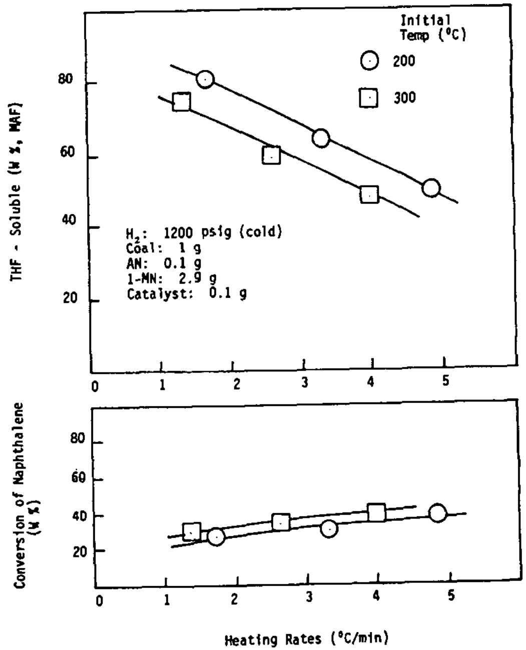

Figure 3

Effects of Heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of DHA, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

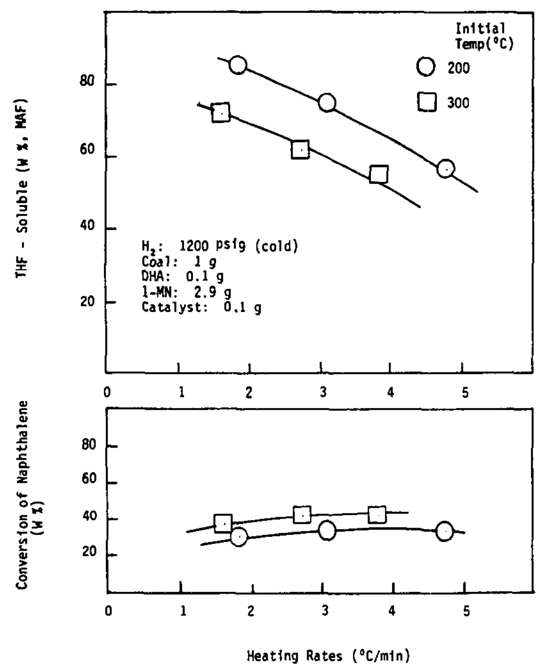

Figure 4

Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of Q, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

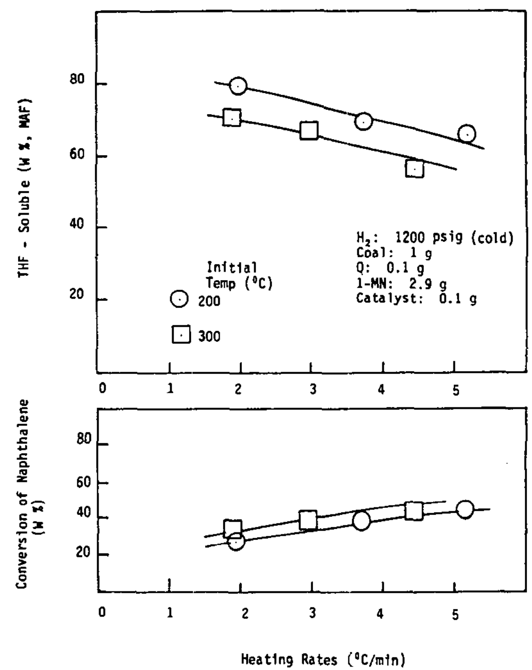

Figure 5

Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of THQ, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

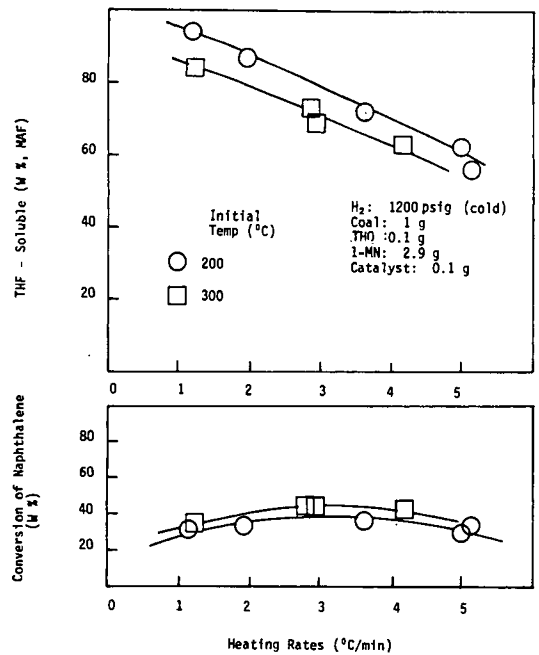

Figure 6

Effects of heating rates on liquefaction of Ky #9 coal in the presence of various HDS and presulfided fresh Shell 324 M catalyst, increasing liquefaction temperatures from 200°C up to 380°C.